Chapter

Introductory Chapter: Zeolites - From Discovery to New Applications on the Global Market

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1. Introduction

From the discovery of zeolites until today, the interest in scientific research and use of this amazing, interesting, and useful material has continuously grown.

Natural zeolites are hydrated aluminosilicate materials. Primary building units (PBUs) are tetrahedra of Si and Al oxides which are interconnected by oxygen ions into two-dimensional and three-dimensional secondary units (secondary building units [SBUs]). The zeolite network consists of channels and cavities filled with hydrated alkali and alkaline earth metal ions. With the presence of these metal ions in the structure of zeolites, a balance between positive electric charge of metal ions and negative charge of zeolite network is achieved.

The hydrating and dehydrating properties of zeolites were crucial in discovering their physical and chemical properties and their wider use, and that is why this mineral was named "boiling stone" (ζέω (zéō) meaning "to boil" and λίθος (líthos) meaning "stone") [1].

Unlike natural zeolites which are formed as crystals in cavities of basalt rocks or as volcanic tuff in different geological environments at relatively low temperatures, synthetic zeolites are created by hydrothermal synthesis in laboratory conditions. During hydrothermal synthesis in the presence of certain chemical compounds ("template" or structure directing agent (SDA)), which act on the organization of SBUs and consequential formation of tertiary or composite building units (TBUs), a final crystal zeolite is created in the form of a polyhedron which contains Si-O-Al bonds. Control of kinetic processes during zeolite synthesis is especially important since most of the zeolites created via this process are metastable phases [2].

2. Zeolite's history

Zeolite materials were discovered in the eighteenth century when a Swedish chemist, founder of modern mineralogy, Baron Axel Fredrik Cronstedt, discovered that during the heating of mineral "stilbite," moisture appears on its surface [3]. His discovery began the research of chemical, physical, and mineralogical characteristics of natural zeolites.

In spite of the limited capabilities of structural research of zeolites at the time of their discovery (unlike today's modern methods), researchers set the foundations for today's application of natural and synthetic zeolites (**Figure 1**). Based on Cronstedt's observations and research, in the middle of the nineteenth century according to the available literature, the first synthetic zeolite-levinite [5] was synthesized, while in the first half of the twentieth century (after the first structural analysis

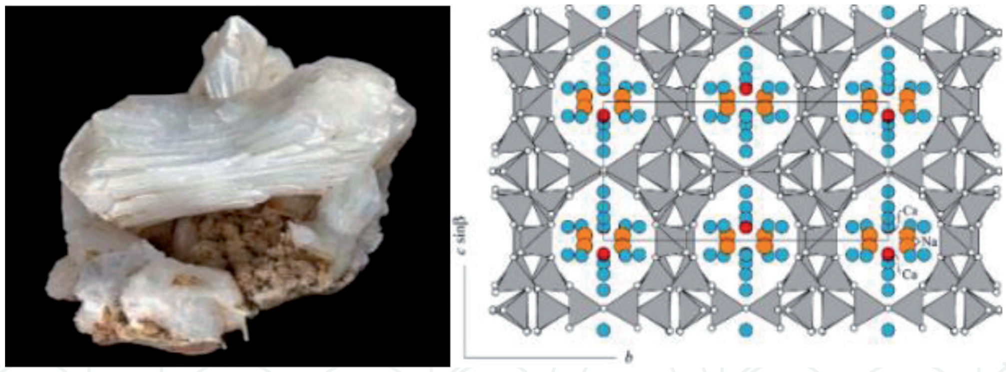

Figure 1.
The mineral stilbite (left) and the crystal structure (framework) of the stilbite group (right) [4].

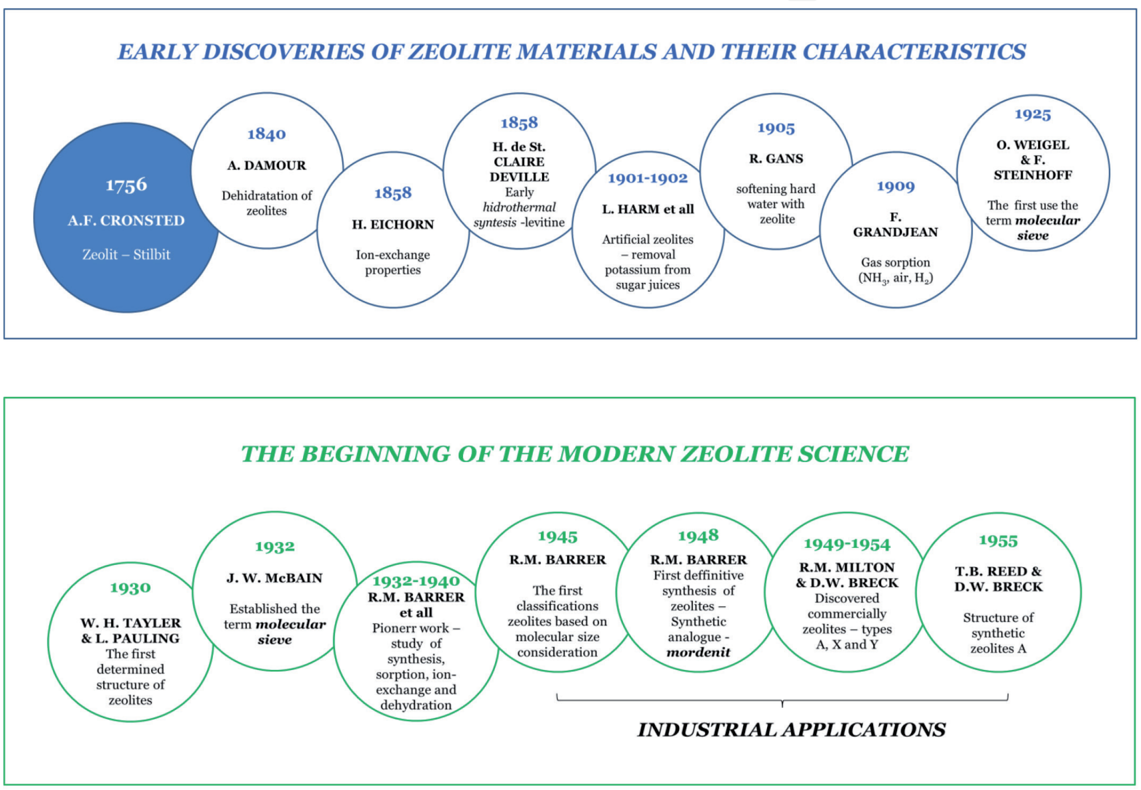

Figure 2.
Early discoveries of zeolite materials and their characteristics, the beginning of the modern zeolite science, and their industrial applications [7, 8].

of zeolite materials), a synthetic analog zeolite-mordenite [6] was synthesized. Intensive research on the synthesis as well as physical and chemical properties of zeolites (absorption, ion exchange, dehydration) enabled the industrial application of zeolites. Significant discoveries and research of zeolites, as well as the beginning of modern zeolite science (parallel with the development of new instrumental techniques), are shown in **Figure 2**.

3. Scientific research and industrial applications of zeolites

Almost three centuries have passed since the discovery of zeolites, and the interest in research of natural zeolite materials has not diminished. Equally, obtaining the optimal properties of synthetic zeolite for their technological application is a priority in scientific research.

In 2007 the sixth edition of "The Atlas of Zeolites" was published, in which the data for each of the 176 unique zeolite framework types are presented [9]. Of the total natural zeolites discovered (more then 60), only six occur in large quantities in the natural deposits worldwide: analcime (ANA), chabazite (CHA), clinoptilolite (HEU), erionite (ERI), mordenite (MOR), and phillipsite (PHI). Ferrierite (FER) occurs in a few large deposits.

Each of the seven natural zeolites has been synthesized, but only mordenite and ferrierite are synthesized in large quantities (synthetic mordenite has large pores while natural mordenite has small pores) [10].

Commercial natural zeolite deposits are primarily found in the USA (volcanic tuffs in saline, alkaline lake deposits, and open hydrologic systems). If both natural and synthetic zeolites are equally available in commercial quantity, synthetic zeolite will be more acceptable because the process of removing impurities from natural zeolite is significantly more expensive.

Even though there is a large number of scientific research which describes properties, structures, characteristics, physical and chemical processes of absorption, and ionic exchange of zeolites with the use of modern techniques, still some of the properties and processes are not completely understood, especially the ones related to natural zeolites. Still there is room for further research and application of these incredible microporous materials in areas which are still unexplored.

Zeolites have found application in almost all areas of agriculture and animal husbandry, biotechnology, medicine, chemical industry, construction industry, oil and natural gas industry, water processing, etc., as well as new technologies which contribute to sustainable development. Due to their specific properties, high thermal and hydrothermal stability, as well as environmental acceptability, zeolites are an alternative to similar materials that are not economically and environmentally acceptable [11–34].

Since the first industrial applications (during the beginning of the twentieth century) until today, demand for zeolites has permanently grown, whether they are used individually or in combination with other micro- and nanoporous materials. New scientific research of synthetic zeolites contributes to the further development of highly active and selective synthetic zeolites used as catalysts, adsorbents, and ion exchangers with high capacity and selectivity.

The increasing number of national and world technological innovation (patents) allows the new industrial applications of zeolite materials, which positively affect economic growth and development with the emphasis on zeolite materials that do not pollute the environment [35, 36].

3.1 Global zeolite market

Zeolite markets (natural and synthetic products) are developed on all continents, shown in **Figure 3**. The largest market of zeolites is in the USA, followed by the Asia-Pacific area, China, India, Europe, and other markets.

Global zeolite market share (by products) shows that the synthetic zeolites have a bigger share than the natural zeolites (**Figure 4**).

In 2016 the zeolite global market was estimated at 29.08 billion USD with an expected growth of 2.5% in the period from 2016 to 2022. Therefore, zeolite global market could achieve a value of 33.8 USD until 2022 [37].

Market research companies have published reports in which the following are presented: zeolite market size, share, and trends analysis report by product, by application, and by region, for the specific estimated period. Some of their data are shown in **Table 1**. The value of compounded annual rate of growth (CAGR) is referring to the valuation before the COVID-19 pandemic.

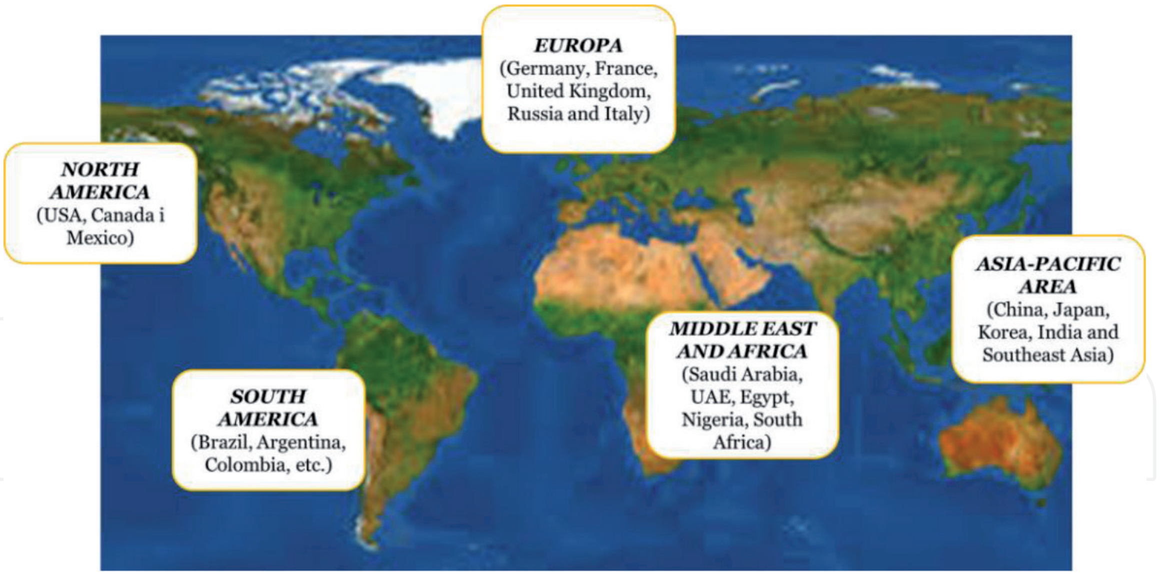

Figure 3.
Zeolite market segmented by continents.

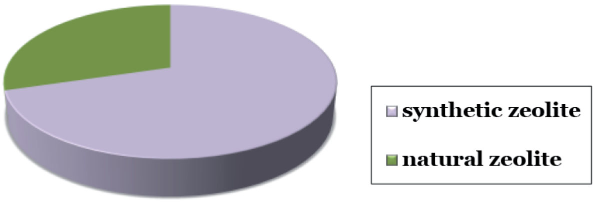

Figure 4.
Global zeolite market share (by products).

Natural and synthetic zeolite/application	Zeolite market size	Forecast period	CAGR	Ref. (*MRC)
High-quality transportation fuels and chemical products	4.15 billion USD	2019–2024	5.3%	[39]
Membrane	**NA	2017–2025	3.7%	[40]
Paints and coating industry	53.4 million USD	2016–2024	3.2%	[41]
Detergents	1.4 billion USD	2018–2028	2.6%	[42]
Adsorbents, ion exchange, catalyst	**NA	2019–2026	2.73%	[43]
Cement, animal feed industry, wastewater treatment	6.6 billion USD	2019–2026	4.9%	[44]
Synthetic zeolite market	19.81 billion USD	2017–2025	4.6%	[45]

*MRC, market research company.
**NA, not available.

Table 1.
Estimation of global zeolite markets growth (data were taken from market research company reports).

Estimations of market research companies are that the market of natural zeolites will have slower growth until the year 2030, considering limitations such as the high price of raw materials, high costs of transportation of raw materials, and availability of alternative materials in specific areas of industrial application (such as enzymes, metals, and other chemical compounds in catalysis processes). However, natural zeolites hold an advantage over other materials because they are nontoxic and ecologically acceptable and as such materials can meet the demands which are set by environment protection laws.

Unlike natural zeolites, the demand for synthetic zeolites until the year 2030 is estimated to grow in areas of industrial application [38].

Global markets depend on a series of factors such as political and economic situations as well as other factors that cannot be influenced or predicted. One such factor is the COVID-19 pandemic which (according to first forecasts) caused a change in market conditions and slowed down technological progress and the start of new production, as well as made launching new products on the market based on zeolite materials harder.

4. New challenges in research and application of zeolites

Today, the humankind is faced with many threats such as (i) drought and lack of freshwater caused by climate change, (ii) political and economic instabilities, and (iii) dangerous pandemics such as the SARS-CoV-2 pandemic, which caused slowing down of scientific research, economic growth, and development and even brought into question the survival of mankind.

With current use of zeolites in agriculture, animal husbandry, water processing, numerous industries (chemical, oil, construction, etc.) biotechnology, medicine, etc., the future of zeolite application opens up new possibilities for research, development, and technological application in still undiscovered areas such as medication and antimicrobial application [46], which would allow new global markets for zeolites.

Furthermore, the application of zeolites in technologies that can contribute to the reduction of CO2 emissions (one of the greenhouse gases which contributes to climate change) could have a significant role in their future use [47–49].

5. Conclusions

Scientific research of natural zeolites poses a challenge in zeolite science because there are still many unexplored properties of this fascinating, ecologically friendly, and truly useful microporous material. Further research on natural zeolite and production of new synthetic zeolites open up possibilities of their application in still unexplored areas in the near future because their application requires low technical complexity and initial infrastructure investment.

Conflict of interest

The authors declare no conflict of interest.

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